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Multiple layer sheet material, packages and methods of making packages.

Abstract:

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(A2) Sheet materials and packages made therefrom, and capable of holding hard-to-hold products such as methyl salicylate and other volatile components, in one form include a foil layer (12) and a layer (14) of EVOH between foil layer (12) and the enclosed product. A carboxy-modified adhesive layer (18) is disposed between the EVOH layer (14) and the product. Additional layers (28, 30, 32, 34, 36, 38, 40) are used in the sheet material for purposes of adhesion, appearance, protection, body, and the like. A coextruded film structure comprises an EVOH layer (514), a surface layer (516), an intervening adhesive layer (518), and a fourth covering layer (519) for covering and protecting the EVOH layer (514), especially from physical abuse. Packages made from the sheet materials and coextruded film can be in the form of sachets, pouches and bags, or in the form of dispensing tubes.

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(54) Multiple layer sheet material, packages and methods of making packages.

(57) Sheet materials and packages made therefrom, and capable of holding hard-to-hold products such as methyl salicylate and other volatile components, in one form include a foil layer (12) and a layer (14) of EVOH between foil layer (12) and the enclosed product. A carboxy-modified adhesive layer (18) is disposed between the EVOH layer (14) and the product. Additional layers (28, 30, 32, 34, 36, 38, 40) are used in the sheet material for purposes of adhesion, appearance, protection, body, and the like. A coextruded film structure comprises an EVOH layer (514), a surface layer (516), an intervening adhesive layer (518), and a fourth covering layer (519) for covering and protecting the EVOH layer (514), especially from physical abuse.

Packages made from the sheet materials and coextruded film can be in the form of sachets, pouches and bags, or in the form of dispensing tubes.

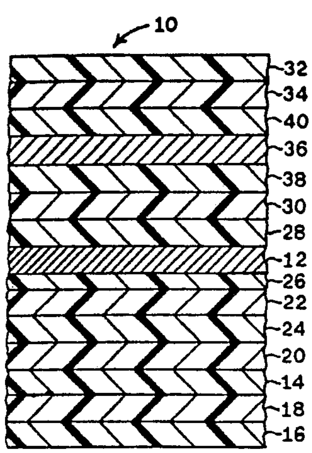

FIG. 1

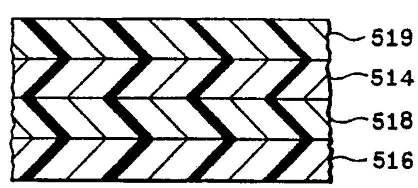

FIG. 5

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MULTIPLE LAYER SHEET MATERIAL, PACKAGES AND METHODS OF MAKING PACKAGES

This invention relates to multiple layer sheet material, packages and methods of making packages.

More particularly, the invention pertains to laminated sheet materials used for packaging. Sheet materials are commonly known for their use in making bags, pouches, and tubes, and the sheet materials of the present invention can be used for making any of these types of packages. The description hereinafter will, by way of example only, be addressed primarily to sheet materials as they relate to packaging products in lap seamed tubes.

Laminated sheet materials of the variety disclosed herein, and especially those containing a layer of metal foil, have been used for packaging such materials as toothpaste, foods, and certain chemical compounds. These remain certain products which have not heretofore been packaged in multiple layer sheet materials of the general type disclosed herein because of the package's susceptibility to being chemically attacked by the products. Particularly troublesome, and addressing now the problem addressed by the inventors herein, are those compounds which use especially volatile, and chemically active, materials such as methyl salicylate.

Conventional sheet materials contain a barrier layer of aluminium foil, and protective, covering, sealing, bonding and the like layers of polymeric materials on both sides of the aluminium foil. It has been found unsatisfactory to package products containing methyl salicylate in known sheet materials of this type because methyl salicylate penetrates through the intervening polymeric layers and attacks the interfacial adhesion on the product side of the metal foil layer. The attack on the metal foil interfacial adhesion is effective to cause delamination of the sheet material, and subsequent failure of the package.

There are a number of advantages to the laminated type of sheet material according to the invention over the conventionally used packages of metal foil. The conventional tubes of metal foil, which are used for packaging these hard-to-hold products, have a number of disadvantages. Among the disadvantages are the thickness of the metal foil which is used, and its associated tendency to crack upon repeated flexing. Metal foil tubes are also expensive. While such disadvantages have been known for quite some time, there has not, in the past, been a satisfactory substitute material for use in packaging the hard-to-hold materials such as those containing methyl salicylate.

It would be highly desirable if a functionally acceptable material could be devised which can be used to package materials which attack the more conventional multiple layer sheet materials which are used in packages of this type.

This invention aims, inter alia, to provide multiple layer sheet materials, capable of holding such a volatile material as methyl salicylate, which sheet materials possess metal foil layers to provide a high barrier to the transmission of product components through the package wall.

The invention seeks to devise a multiple layer sheet material capable of holding products containing certain volatile materials, without delaminating, over the typical life of the product. Clearly, by devising a multiple layer sheet material capable of holding products containing methyl salicylate and similar materials for the expected shelf life of the product without significant loss of any of the volatile components, resulting changes in the product composition are substantially avoided.

A preferred embodiment of the invention is a sheet material which comprises at least five layers. The first layer is comprised of a metal foil, preferably aluminium foil, having a first, primed surface and a second surface opposite the first, primed surface. A second layer, of ethylene vinyl alcohol, has a first surface disposed toward the first foil layer and a second surface disposed away from the foil layer. A third, adhesive means between the first and second layers adheres those layers to each other. A fourth, protective layer is disposed on the second surface of the first or foil layer, to provide protection of the foil from physical abuse. A fifth, covering layer is disposed on the second surface of the second or ethylene vinyl alcohol layer. Preferably the fifth layer is composed of a heat sealable polymer such as linear low density polyethylene. Linear low density polyethylene is a copolymer of ethylene and an α-olefin containing at least three carbon atoms, and is available from, for example, Dow Chemical Company.

The adhesive means preferably comprises one or more layers of material which are capable of bonding the first layer of foil to the second layer of ethylene vinyl alcohol. The adhesive means preferably comprises four separate components. The first component is a layer of ethylene acrylic acid adhered to the first surface of the foil layer through a second component of a primer containing a chromium complexed polyacrylic acid. The second component primer comprises the surface priming on the first layer of metal foil. The third component is an anhydride modified polymer containing an olefinic base resin such as a polyethylene or a polyethylene copolymer, especially linear low density polyethylene. The third component of the adhesive means is bonded to the first surface of the EVOH layer. The fourth component of the

preferred adhesive means is a layer of low density polyethylene disposed between the olefinic adhesive on the EVOH and the EAA.

A sixth layer of adhesive is preferably disposed between the second sand fifth layers of the sheet material. The olefinic adhesive layer between the second ethylene vinyl alcohol layer and the low density polyethylene layer of the third adhesive means can be considered a seventh layer of the sheet material.

In preferred embodiments, the overall thickness of the sheet material is between 0.1 and 0.6 mm.

With respect to the ethylene vinyl alcohol of the second layer, it is preferred that the vinyl alcohol component comprise 55 mole percent to 72 mole percent vinyl alcohol moieties, most preferably 60 mole percent to 64 mole percent. If the alcohol content is below the preferred range, the barrier to transmission of a volatile component such as methyl salicylate is reduced, and the layer of ethylene vinyl alcohol required to provide an equivalent barrier would have have to be undesirably thickened in order to provide the necessary level of total barrier to the methyl salicylate transmission. If the vinyl alcohol component is increased above the preferred range, the extrusive properties of the ethylene vinyl alcohol copolymer are adversely affected to the point that the extrusion process becomes difficult. Also the adhesive capabilities of the EVOH layer may be adversely affected by increased amount of alcohol in the EVOH layer. Additionally, the ethylene vinyl alcohol layer may be undesirably brittle.

It is preferred that the fifth or covering layer be polymeric and that the sixth adhesive layer between the second, ethylene vinyl alcohol layer and the fifth, covering layer comprise a base polymeric resin, preferably an olefin resin, and anhydride comprising active anhydride component equivalent to between about 0.10% and about 0.60% by weight maleic anhydride. Preferably, the anhydride modification is between 0.26% and 0.40% (equivalent) of the weight of the composition, and most preferably between 0.30% and 0.36% of the overall weight of the composition of the adhesive polymer. It is preferred that the composition of the sixth adhesive layer have a melt index at 210 °C of between 3 and 9, preferably between 5 and 7. Further, in some cases the sixth layer may include, in addition to the base resin and the anhydride component, up to 15%, preferably up to 10% of an elastomeric material.

It is preferred that the polymeric composition of the fifth layer and the base resin of the sixth layer both comprise linear low density polyethylene copolymers.

In preferred embodiments of the invention, the composition of the seventh layer comprises the composition of the sixth layer.

From another aspect a sheet material according to the invention comprises essentially a five layer coextruded film containing outer surface layers of low density polyethylene and linear low density polyethylene, a core layer of ethylene vinyl alcohol, and adhesive layers, on either side of the ethylene vinyl alcohol layer, intervening between the ethylene vinyl alcohol and the respective surface layers. The five layer sheet material of this embodiment corresponds essentially to five layers of the previously recited embodiment which contains the metal foil. Those five layers are the five outermost layers of the sheet material, which five layers include the surface layer of linear low density polyethylene. The same parameters and limitations as described above apply to the five layer sheet material. That sheet material may be made, and preferably is made, by a coextrusion process.

Any of the sheet materials of the invention, including the five layer sheet material, and the more complex sheet structure containing metal foil, may be used to make packages for containing chemically active products, and especially active products having components having a high level of chemical activity in combination with the high level of volatility of at least one component.

The sheet materials of the invention include a sheet material comprising, from the inside surface thereof in the package outwardly a first layer of a polyolefin; a second adhesive layer comprising a polyethylene and about 0.10% to about 0.60%, preferably about 0.26% to about 0.40% (equivalent) of an anhydride, and having a melt index at 210 °C of between 3 and 9; and a third layer of ethylene vinyl alcohol, the packaging sheet material being functional to retard transmission of the volatile component of, for example, methyl salicylate, acetone, acetic anhydride, undecylenic acid, ichthamnol coal tar derivative, or polyurethane prepolymer, through the sheet material, sufficient to provide for acceptable compositional stability of the volatile component in the product over the normal shelf life of the product. The composition of the first layer may, in some cases, be based on propylene. In other cases, it may be based on ethylene. Further, it may be based on a combination of ethylene and propylene. Preferably it comprises a copolymer of ethylene and up to 10% of an alpha olefin, having a carbon chain at least three carbon atoms long, and commonly referred to as linear low density polyethylene.

The invention further provides a method of making a package which comprises fabricating the sheet material by adhering a first layer of a covering to a second layer of metal foil, and on the surface of the foil opposite the first layer, adhering, by use of intervening adhesive means, a coextruded film structure comprising 3 or more layers and including a heat sealable layer on the surface thereof opposite the foil

layer, the coextruded film structure being between 0.05 mm and 0.25 mm thick. The method further comprises fabricating the sheet material into a package enclosure by forming a tube comprising a lap seal, and with one end or even both ends of the tube open. The method further comprises placing a product in the package and closing and sealing the one end (or both ends) to complete the fabrication, filling, and sealing of the package. The method is especially advantageous where the product contains a component capable of attacking the metal foil layer and wherein the coextrude film structure includes a layer of ethylene vinyl alcohol comprising at least about 55% vinyl alcohol, and no more than about 72% vinyl alcohol, and an adhesive layer on one surface of the ethylene vinyl alcohol layer. The adhesive layer comprises polyethylene as a base resin and about 0.10% to about 0.60%, preferably about 0.26% to about 0.40% anhydride (equivalent), the adhesive layer having a melt index, at 210 °C, of between 3 and 9.

In fabrication of typical packages, portions of the sheet material are folded onto each other in a tubular configuration in formation of a lap seam, wherein an upper surface of an underlying layer is in facing contact with a lower surface of an overlying layer. A seal is fabricated by means of heating the sheet materials such that the upper surface of the underlying layer is bonded to the lower surface of the overlying layer.

In another construction useful in making packages of sheet material of the invention, the same general container shape may be fabricated using fin seals wherein portions of the same surface are brought into facing contact with each other to make the closure seals.

In still other cases, the sheet material of the invention may be used in combination with other sheet structures to fabricate less than the entire package structure. In these cases, the sheet material of the invention is typically seen as a closure, cover, or other type of lid material which is bonded to a second, and different packaging sheet material, such as a preformed rigid tray.

Another way of considering the invention is that it provides, in two layers, one of ethylene vinyl alcohol and the other of the anhydride modified polyethylene composition, preferably linear low density polyethylene, a composite barrier structure capable of holding products having one or more of the recited hard-to-hold components.

Packages according to the invention are entirely satisfactory and are preferred for packaging products having volatile components. Especially the packages made with the sheet structures containing the metal foil layer are desirably used for packaging products which have, in their composition, components which exhibit both the properties of high levels of chemical reactivity and high levels of volatility, or which are sensitive to exposure to light.

Embodiments of the invention will now be described by way of non-limitative example in the following description which is to be read in conjunction with the accompanying drawings, in which:

FIGURE 1 is a cross-section through one sheet material according to the invention;

FIGURE 1A shows a corss-section through a prior art sheet structure;

FIGURE 2 shows a side-view of a typical tube package made with sheet materials according to the invention;

FIGURE 3 is a cross-section of the tube taken at 3-3 of FIGURE 2;

FIGURE 4 is a cross-section of a typical fin-sealed package according to the invention; and

FIGURE 5 is a cross-section of a less complex multiple layer film according to the invention.

Referring to FIGURE 1, there is seen a cross-section of sheet material 10 representative of a sheet material of the invention. With respect to preventing the transmission of volatile product components through the packaging sheet material, it is important in some embodiments to provide a layer of metal foil 12 which serves as a barrier to transmission of many components. The interfacial adhesion on the product side of metal foil 12, however, is susceptible to being attacked by the more chemically aggressive components of some of the material which may be packaged. Thus it is important in some cases to provide protective materials between the metal foil layer 12 and that surface which in the package, is an interior surface in contact with the product.

With respect to protecting the interfacial adhesion at metal foil layer 12, there is provided, in the FIGURE 1 embodiment, a layer 14 of ethylene vinyl alcohol (EVOH), a layer 16 of linear low density polyethylene (LLDPE) on the surface of the sheet material, and a layer 18, between layers 14 and 16, of an adhesive polymer having a base resin of linear low density polyethylene and an anhydride modification.

Between the EVOH layer 14 and foil layer 12, there is provided a second adhesive layer 20, an adhesive layer 22 of ethylene acrylic acid (EAA) or ethylene methacrylic acid (EMAA), and a layer 24 of a low density polyethylene (LDPE) interposed between layers 20 and 22. A chromium complexed primer, shown as layer 26 between foil layer 12 and layer 22 improves the adhesion between the foil and layer 22. A second layer 28 of EAA or EMAA is on the other surface of foil layer 12, and serves as a bonding site for

the adjacent layer 30 of LDPE.

Layer 32 of LDPE is on the outside surface of the sheet material, and layer 34 of pigmented low density polyethylene is adjacent layer 32. Layer 36 of paper is bonded to LDPE layers 30 and 34 by primer, shown as layers 38 and 40, of polyethylene imine (PEI) primer.

FIGURE 2 shows a tube package 42 made with the sheet material 10 of the invention. Sheet material 10 is used especially to make the sidewalls 44 of the tube. The sidewall 44, made from sheet material 10, is used in combination with the head 46 and the cap 48 in fabrication of the tube package.

FIGURE 3 shows a cross-section of the tube of FIGURE 2; and especially shows the typical method of joining the edges of the sheet material in fabricating the lap seam 50 which is formed along the length of the tube in joining the two edges of the sheet material to each other. FIGURE 3 also shows the positioning of the packaging sheet material 10 of the tube relative to the product 52 contained therein.

FIGURE 4 shows a cross-section of an alternate construction for packages of the invention. In the construction illustrated in FIGURE 4, the closure of facing elements of the packaging material is made by means of fin seals 54, rather than by lap seals as at 50 in the tube of FIGURE 3.

While the embodiments shown in FIGURES 1-4 are characteristic of the preferred embodiments of the invention, there is also seen to be novelty and utility in a simpler depiction of the invention as shown in the sheet structure of FIGURE 5. With respect to the numbering of FIGURE 5, the last two digits of the layer numbers in FIGURE 5 correspond to the two digit numbers given for similar layers in FIGURE 1. Thus layer 514 is EVOH. Layer 516 is LLDPE. Layer 518 is an adhesive comprising a base resin of LLDPE and an anhydride modifier. Layer 519 is a covering layer over layer 514, and is provided primarily for the purpose of physically protecting the EVOH in layer 514, though layer 519 may also serve other functions as well.

Returning now to FIGURE 1, and a detailed discussion of how each of the layers participates in the functioning of the sheet materials and packages of the invention. As stated earlier, the invention seeks to provide sheet materials and packaging which are capable of successfully holding aggressive products, and especially those which have volatile and chemically active components. An especially hard to hold material is methyl salicylate. As a starting point directed toward solving the problem of packaging products containing methyl salicylate, the prior art sheet material shown in FIGURE 1A was used to package a product containing methyl salicylate. As shown by the labeling of the layers in FIGURES 1 and 1A, the prior art sheet material of FIGURE 1A was identical to the upper layers of FIGURE 1 of the instant invention. Specifically, the layers common to both FIGURE 1 and FIGURE 1A are layers 12, 22, 26, 28, 30, 32, 34, 36, 38 and 40. When a methyl salicylate product was packaged in tubes made from sheet materials of FIGURE 1A, the sheet material showed attack at the foil interface, evidenced by delamination of the sheet material, resulting in failure of the package to hold the product.

It appeared that the failure of the package was related to attack on the interfacial adhesion between foil layer 12 and EAA layer 22/primer 26. Thus began the search for a means to protect the foil interface from attack by the methyl salicylate. After substantial amounts of testing and evaluation, it was discovered that a single layer film of EVOH provided what appeared to be an acceptable barrier to the transmission of methyl salicylate. And thus began the attempt by the Applicant to incorporate the EVOH into the sheet material in such a way that the foil interface would be protected from attack by the methyl salicylate. To that end, experimental sheet materials were made incorporating the EVOH into the sheet material.

With respect to the layers between foil layer 12 and the outside layer 32 of the sheet material, there is no particular criticality to the sequence or composition of those layers in obtaining the foil-protecting barrier properties important to the sheet material herein. That composite of layers is shown with respect to its preferred structure. Rather, the structuring of the sheet material on that outer side of foil layer 12 is independent of the structuring with respect to providing the barrier function for protecting foil layer 12 from attack by the product. Those outer layers serve such purposes as protecting foil layer 12 from physical abuse from outside the package, for providing bulk or body to the film, for graphics, color, etc., and other means for effecting the appearance of the package. Thus their selection is made by the sheet material designer independent of the objective of protecting the foil interface from attack by chemicals in the contained product 52. Thus, in the search for a means to protect the foil interface from attack by the components of the product, various materials were added to the base prior art sheet material shown in FIGURE 1A for the purpose of providing a barrier functional for the protective purpose intended.

Since it had been discovered that EVOH by itself serves as a functional barrier to the transmission of methyl salicylate, an initial attempt was made to provide a layer of EVOH between the metal foil layer 12 and the product. To this end a five layer film, coextruded by the cast coextrusion process, was laminated to the inner layer (22 of the base sheet structure represented by the prior art structure of FIGURE 1A). The coextruded film which was laminated at layer 22 was as follows:

EAA/ADH/EVOH/ADH/LLDPE (Experiment W)

The adhesive on both sides of the EVOH was Admer NF-500, an anhydride modified adhesive material based on LLDPE. The EVOH had a vinyl alcohol content of 66 mole percent. The five layer coextruded film was 0.09 mm. thick. The EAA layer of the five layer coextruded film was bonded to the EAA layer corresponding to layer 22 in FIGURES 1 and 1A. This film provided good adhesion at the foil layer, with fair adhesion between the EVOH layer 14 and the adhesive layers. The film delaminated at the EVOH/adhesive interface when methyl salicylate-containing product was stored in a package made with it. In another variable, an additional layer of LLDPE was added to the inside surface of the package. This structure, too, was not able to hold the methyl salicylate-containing product.

In another series of tests, oriented polyester was incorporated into the film in combination with the EVOH coextrusion. In this experiment, the EAA layer 22 was omitted. A layer of oriented polyester 0.012 mm thick was adhesive laminated directly to layer 12 of the foil using polyester urethane curing adhesive. The same five layer coextruded film was then adhesively laminated to the polyester using a second polyester urethane curing adhesive. Finally a layer of EAA was attached to the LLDPE surface of the coextruded film to complete the sheet structure for the trials. The final structure of the sheet material was as follows:

outer composite / foil / 4147 ADH / polyester / 5133 ADH / EAA / ADH 500 / EVOH / ADH 500 / LLDPE / EAA /

(Experiment X)

A second, similar structure was made using a third polyester urethane curing adhesive, as follows:

outer composite / foil / 7900 ADH / polyester / 7900 ADH / EAA / ADH 500 / EVOH / ADH 500 / LLDPE / EAA /

(Experiment Y)

These materials also failed to successfully hold the methyl salicylate product.

While the initial testing of EVOH had indicated that it provided a good barrier to transmission of methyl salicylate, the initial attempts to incorporate EVOH into the sheet material and thereby provide functional protection for the foil layer 12 had failed to live up to their expectations. Thus the pursuit of the solution then headed in a direction away from EVOH. Additional sheet materials were made with polyester, which had also, in separate tests, shown a good barrier property for methyl salicylate. These too failed. Attempts were made with certain epoxies. These too failed.

Improvement was finally obtained with a coextruded structure fabricated by the tubular water quench coextrusion process. The structure was 0.09 mm. thick, and was arranged as follows:

LDPE Adh 220/EVOH/Adh 220/LLDPE (Experiment AW)

The LDPE and EVOH layers were each 20% of the thickness. The two adhesive layers were each 10% of the thickness. The LLDPE layer was 40% of the thickness. The adhesive 220 was a low density polyethylene based adhesive containing about of 0.14% maleic anhydride, according to the manufacturer.

After storage testing with a methyl salicylate product, the packaging material had a peel strength of about 335 grams per cm. width.

A still strong packaging structure was made using the following five layer structure, coextruded by the tubular water quench process.

LDPE Adh 550/EVOH/Adh 550/LLDPE. (Experiment AX)

The overall 5-layer structure was 0.09 mm. thick. The LLDPE was about 40% of the thickness. The EVOH and LDPE were each about 20%, and the Adh. 550 layers were each about 10%. These five layers represent layers 24 (LDPE), 20, 14, 18, and 16, respectively and in order, in FIGURE 1. The LDPE side of the coextruded film was corona treated in line with the coextrusion process, and was subsequently extrusion laminated to the foil using EAA layer 22 0.05 mm. thick as the laminant.

Tubes were made with this sheet structure, filled with product containing methyl salicylate and storage tested for up to 3 months at up to 49° C. The tubes wer 1.9 cm. diameter, 6.7 cm. in length. The tubes were tested periodically, and at the end of the test, for interlayer adhesion, and for seal integrity along

longitudinal lap seam 50. The testing showed that the lap seam remained in good condition, and the sheet material could not be separated at any interface between the foil layer 12 and the product contact LLDPE layer 16.

Experiment AX was repeated as Experiment "AX-2" but the corona treatment was done out-of-line between the extrusion fabrication process and the extrusion lamination process.

Additional experiments were then conducted to further define the invention. Five layer structures representing layers 24, 20, 14, 18 and 16 were coextruded, with the same thicknesses as in Experiment AX, except as noted, in an air quenched tubular coextrusion process, generally described as "blown extrusion." Table 1 shows these additional structures, with processing and structural differences indicated.

Each 5-layer coextruded structure was extrusion laminated to the base sheet as illustrated in FIGURE 1, using 0.05 mm. of EAA as the extrusion laminant, except as noted, all as previously described for Experiment AX. The base sheets in Experiments W, AT, and AU differed slightly from the others, but the differences were inconsequential to the results of the experimental testing for peel strength and lap seam integrity. The laminated base sheets were formed into lap seamed tubes as in FIGURES 1 and 3. Samples of the tubes filled with the methyl salicylate product were stored at different temperatures, typically 23 °C., 41 °C., and 49 °C. The tubes were examined periodically for interfacial adhesion and lap seam integrity. Table 1 shows the results of the most severe test, namely at 49 °C, except for Experiment AX-2 which represents 41 °C. storage.

TABLE 1

Experiment	Coextrusion Process	Coextruded Structure	Maleic anhydride in Adhesive Layers 18 and 20	Ethylene Content in EVOH	Corona Treatment In-Line, *Dynes*	
W	cast	EAA Adh 500 EVOH - DE Adh 500 LLDPE 2035	0.13%	34%	yes	
AT	TWQ	LDPE Adh 220 EVOH-ET Adh 220 LDPE	0.14%	38%	yes	

Corona Treatment at Extrusion Laminator	Comments	Test Results after Storage at 49°C. for Period Indicated			
		Peel Strength Instron, grams/cm.width			Lap Seam Integrity
		2 mths	3 mths	4 mths	
unknown		D	--	--	--
unknown	Foil staining after 3 1/2 months storage	--	--	--	satis- factory

Experiment	Coextrusion Process	Coextruded Structure	Maleic anhydride in Adhesive Layers 18 and 20	Ethylene Content in EVOH	Corona Treatment In-Line, Dynes	Corona Treatment at Extrusion Laminator
AU	TWQ	LDPE / Adh 220 / EVOH-ET / Adh 220 / LDPE	0.14%	38%	yes	unknown
AW	TWQ	LDPE / ADH 220 / EVOH-ET / ADH 220 / LLDPE 2056	0.14%	38%	yes	yes
AX	TWQ	LDPE / ADH 550 / EVOH-ET / Adh 550 / LLDPE 2056	0.32%	38%	yes	yes

Comments	Test Results after Storage at 49°C. for Period Indicated			
	Peel Strength Instron, grams/cm.width			Lap Seam Integrity
	2 mths	3 mths	4 mths	
Extrusion laminant was coextrusion of .038 mm. LDPE and 0.013 mm. EAA, with EAA toward the foil. staining after 3 1/2 months storage.	--	--	--	satis-factory
	NM	NM	335	good
Peel Strength CNS at both 6 weeks and 3 months	NM	CNS	NM	good

Experiment	Coextrusion Process	Coextruded Structure	Maleic anhydride in Adhesive Layers 18 and 20	Ethylene Content in EVOH	Corona Treatment In-Line, Dynes
AX-2	TWQ	Same as AX	0.32%	38%	no
AZ	Blown	Same as AX	0.32%	38%	38
BA	Blown	Same as AX	0.32%	38%	38
BB	Blown	Same as AX	0.32%	38%	no
BC	Blown	LDPE Adh 500 EVOH-ET Adh 500 LLDPE 2056	0.13%	38%	38

Corona Treatment at Extrusion Laminator	Comments	Test Results after Storage at 49°C. for Period Indicated			
		Peel Strength Instron, grams/cm.width			Lap Seam Integrity
		2 mths	3 mths	4 mths	
no	Corona treated to 42 dynes, out of line, between extrusion process and extrusion laminating process. Storage for test purposes was at 41°C.	NM	236	NM	
yes		441	NM	268	good
no		504	NM	311	good
yes		331	NM	181	good
yes		382	NM	260	good

:xperi-ment	Coextrusion Process	Coextruded Structure	Maleic anhydride in Adhesive Layers 18 and 20	Ethylene Content in EVOH	Corona Treatment In-Line, Dynes
BD	Blown	LDPE-EX Adh 550 EVOH-ET Adh 550 LLDPE-EX	0.32%	38%	40
BE	Blown	LDPE-EX Adh 550 EVOH-ET ADH 550 LLDPE-EX	0.32%	38%	41

Corona Treatment at Extrusion Laminator	Comments	Test Results after Storage at 49°C. for Period Indicated			
		Peel Strength Instron, grams/cm.width			Lap Seam Integrity
		2 mths	3 mths	4 mths	
yes		445	NM	283	good
yes	Same as BD, except EVOH layer was 10% of thickness. LDPE layer was 25% and LLDPE was 45%.	409	NM	205	good

Experiment	Coextrusion Process	Coextruded Structure	Maleic anhydride in Adhesive Layers 18 and 20	Ethylene Content in EVOH	Corona Treatment In-Line, Dynes
BF	Blown	LDPE-EX ADH 550 EVOH-ET Adh 550 LLDPE-EX	0.32%	38%	41
BG	Blown	LDPE-EX ADH 550 EVOH-N Adh 550 LLDPE-EX	0.32%	29%	40

Corona Treatment at Extrusion Laminator	Comments	Test Results after Storage at 49°C. for Period Indicated			
		Peel Strength Instron, grams/cm.width			Lap Seam Integrity
		2 mths	3 mths	4 mths	
yes	Same as BD, except EVOH layer was 30% of thickness. LDPE layer was 15%, and LLDPE layer was 35%.	350	NM	228	good
yes		335	NM	268	good

D = Delaminated
NM = Not Measured
LDPE and LLDPE are from Dow Chemical Company except as noted
LDPE-EX and LLDPE-EX are from Exxon Chemical Company
TWQ = tubular water quench
Adh 220 has a low density polyethylene base resin.
Adh 500 and 550 have linear low density polyethylene base resins.
CNS = CANNOT SEPARATE

The coextruded film can be as little as about 0.035 mm. thick, up to about 3 mm. thick, with a preferred range of about 0.05 mm. to about 0.75 mm. Flexible films are preferably up to about 0.25 mm or 0.30 mm thick.

The maleic anhydride content as reported herein is determined using Fourier Transform Infrared Spectroscopy. Samples are prepared by pressing the polymer pellets at 190 °C and 4000 psi (276 bar) for 2 minutes to produce a film approximately 0.15 mm. thick. The infrared spectrum in the region around 1790 cm^{-1} is measured for each film and the absorbance of the 1790 band is recorded. The thickness of each sample film is measured and the ratio of absorbance at 1790 to thickness of the film is compared to a calibration curve produced using maleic anhydride standards.

Throughout this teaching, the anhydride content is taught in terms of the maleic anhydride content, since the preferred anhydride is maleic anhydride. It is contemplated that other anhydrides will function similar to maleic anhydride, so long as the layer composition contains an amount of active anhydride which is equivalent to the amount of anhydride contained in the recited amounts of maleic anhydride.

Sheet materials of the invention are capable of holding products containing active carboxy or sulfoxy groups, such as methyl salicylate, acetic anhydride, acetone, undecylenic acid, ichthamnol and polyurethane prepolymers.

The fabrication of the sheet material of FIGURE 1 requires some laminating processing. However, to the extent coextrusion processing can be used, the cost of the fabrication can be minimized. It is seen to be especially desirable to coextrude the 5-layer substructure comprising layers 14, 16, 18, 20, and 24. The specific materials for the several layers are chosen, within the family of resins disclosed for each recited layer, such that they will have rheological properties compatible with the coextrusion process. In that regard, it is desirable that the compositions of adhesive layers 18 and 20 have melt indexes, at 210 °C., of between 3 and 9, preferably between 5 and 7.

A preferred process for coextrusion of the 5-layer substructure is a liquid quench coextrusion process, and preferably tubular water quench. The quench water temperature may be as high as 60 °C, but is preferably lower, such as 30 °-35 °C.

Another, less preferred, process is the blow tubular coextrusion process wherein the extrudate is cooled by a gaseous medium such as room temperature air.

The outer surface of the LDPE layer which is to become layer 24 in the assembled sheet material is preferably corona treated in line with the coextrusion process, to a level of about 42-48 dyness. The sheet material of FIGURE 1 is then assembled by lamination of the 5-layer coextruded film to the previously formed laminate (as seen in FIGURE 1A) by combining the two subassemblies by heat and pressure in a hot nip.

In a less preferred process variation, the corona treatment may be omitted at the coextrusion step, and performed at another time prior to lamination, such as inline with the hot nip lamination. However, this treatment process is less efficient than the preferred in-line treatment at the coextrusion step.

The EVOH of layer 14 has an ethylene content of no more than 45%, preferably at least 28%, most preferably at least 32%. While higher levels of ethylene in the EVOH make the composition more flexible and pliable, at least a part of the barrier property appears to be provided by the vinyl alcohol content, and thus at least 55% vinyl alcohol is preferred with a maximum vinyl alcohol content of about 72%, preferably about 64%, such that the EVOH composition will have facile processability in the extrusion process. Layer 20 is an adhesive composition having the capability to adhere EVOH layer 14 to LDPE layer 24. While it is desirable to have the composition of layer 20 be the same as the composition of layer 18, and same is most economical in provision of coextruded films as shown in FIGURE 5, adhesive layer 20 may be selected to have a different composition. For example, adhesive layer 20 may have a lower anhydride modification level than layer 18, or it may have a different base resin composition such as LDPE, and especially different rheological properties, in order to improve its adhesion to layer 24.

Layer 26 is a primer which is applied to foil layer 12 in order to enhance the adhesion of the foil to the coextruded film. A preferred primer is the conventionally known chromium complexed polyacrylic acid primer. The EAA layer 22 serves the primary adhesion function between foil layer 12 (through primer layer 26) and LDPE layer 24 of the five layer coextruded film.

We refer now to the layers on the outside of the sheet structure from foil layer 12, and namely those layers between foil layer 12 and LDPE layer 32. While those layers are conventional in that they are used as the outer layers in conventional sheet materials used for making squeezable tubes, a discussion of their purpose and function will aid in understanding the overall sheet structures of the preferred embodiments. Layer 28 provides an adhesive function to the foil similar to that of layer 22. LDPE layer 30 provides an adhesive function between layer 28 and paper layer 36, through PEI primer layer 38. PEI primer layer 40 is

also functional in providing enhanced adhesion between paper layer 36 and LDPE layer 34. Typically, layer 34 is pigmented in order to give a desired color and appearance to the outer surface of the package. Finally, LDPE layer 32 is clear and provided the outer and glossy surface of the package.

The outer composite substructure, between layers 28 and 32, provides bulk, appearance, protection of foil layer 12 from physical abuse, and may provide some stiffness or other desirable physical properties to the package. Thus the substructure, including layers 30 and 32, and all the layers in between, could be replaced with other materials comprising one or more layers which provide the desirable functions and properties for the specific product application contemplated.

Turning now to FIGURES 2-4, it is seen that the sheet material shown in FIGURE 1 may be used in fabrication of a tube having a lap seam 50 extending longitudinally along its length. The lap seam is formed by folding a portion of the sheet material onto itself such that a portion of an outside surface layer 32 on an underlying edge of the sheet material is in facing relationship with a portion of an inside surface layer 16 on an overlying portion of the sheet material at the location which forms the lap seam 50. The facing portions of the sheet material are then heated and pressed together such that the polymeric materials in the facing portions flow and bond to form the desired lap seam 50 as shown.

FIGURE 4 shows the cross section of another exemplary package made using sheet materials of the invention. In this embodiment of the packages of the invention, portions of the sheet material 10 are brought into facing relationship to each other with the layer 16 of the corresponding facing portions toward the inside of the enclosure. Heat seals are then fabricated about contiguous portions of the facing portions of the sheet material to make the indicated fin seals 54 seen at FIGURE 4.

FIGURE 5 shows a less complex embodiment of the invention. This embodiment of the invention is useful where the extremely high barrier properties of the foil layer are not necessarily needed. Without the requirement for the foil layer, it is seen that the sheet material can be substantially less complex. Indeed, if covering layer 519 is polymeric, it is possible to make the sheet material at FIGURE 5 by a one step process of coextrusion.

The functional barrier properties of the sheet material of FIGURE 5 are generally provided by the EVOH layer 514, especially concerning barriers to transmission of oxygen and methyl salicylate. Layer 516 provides a substantial barrier to the transmission of moisture, having a moisture vapor transmission rate of no more than about 0.9 grams/645 cm^2-24 hours at 100% relative humidity, preferably no more than 0.9 grams/ 645 cm^2 $^-$ 24 hours. The composition of layer 516, as in layer 16, is preferably based on an olefin polymer or copolymer. A preferred olefin is an ethylene, as polymer or copolymer, but the composition may, alternatively, be based on propylene, butylene (including polyisobutylene) or a combination of the above; or other alpha olefins having a primary monomer containing at least three carbon atoms.

The composition of covering layer 519 may be selected with respect to its capability to serve as a barrier to transmission of a selected material. Its primary function, however, is usually that of protecting EVOH layer 514 from physical abuse when it is used as the outside layer of the package, and from physical attack by the components of the product when it is used toward the inside of the package from layer 514. Indeed, covering layer 519 may include a multiple layer structure including another adhesive layer, such as an adhesive polyethylene, especially a linear low density polyethylene, containing at least about 0.10%, preferably at least about 0.13%, most preferably at least about 0.20% maleic anhydride equivalent, adjacent EVOH layer 514, which represents the same anhydride criteria as for layers 18, 518, and 20. 519 may include other layers of materials which serve to protect or modify, or otherwise enhance, or make more effective, the properties of the EVOH. To that end, and especially with respect to using layer 516 toward the inside of the package, the sheet material of FIGURE 5 is seen to be useful for packaging a variety of products which benefit from the barrier properties of EVOH, yet require substantial levels of adhesion between adhesive layer 518 and EVOH layer 514.

For purposes of this invention, it is necessary that the EVOH have a vinyl alcohol content of at least 55%, preferably at least 60%, in order to provide the primary barrier property to impede the transmission of the methyl salicylate product toward foil layer 12.

It is seen from the previous discussion that adhesive layer 18 includes a chemically modifying component of anhydride for provision of chemical bonding to the EVOH. It may also incorporate therein a material which provides for physical bonding as by a tackifying resin, such as one of the elastomers, which provides for a physical bonding property through tackiness. Typical of elastomers which may be incorporated into layer 18 are polyisobutylene, one of the styrene-blocked olefin copolymers such as styrene butadiene styrene copolymer or styrene ethylene butylene styrene copolymer, one of the diene modified olefins or rubbers such as ethylene propoylene diene monomer terpolymer, an ethylene propylene copolymer such as ethylene propylene rubber, or the like. While low levels of elastomer additive will provide an advantage in some cases, usually 3% to 5% additive is needed in order to provide a discernible

functional improvement. And while up to 25% additive may be used in some cases, usually there is no advantage in using more than 15%, so that is normally a practical upper limit. Layer 20 may be likewise modified.

Most preferred anhydride levels are about 0.26% to about 0.40%. Levels of 0.37% to 0.60% are acceptable for layers 18 and 20, but are not especially preferred. Layer 24 of LDPE is compatible with being adhesively bonded to layer 22 in an extrusion lamination process, as well as to bonding to the adhesive composition of layer 20 in the coextrusion process. Layers 22 and 24 could be combined, or their compositions could be changed, so long as they provide the desired adhesion, or the compatiblization of the adhesiveness between EVOH layer 14 and foil layer 12. Thus layer 24 could be EAA instead of the preferred LDPE, and layer 22 could be EMAA instead of the recited EAA; whereby it is seen that various combinations of materials could provide the desired adhesion.

Thus it is seen that the sheet materials of the invention provide the capability to package chemically aggressive products, including products containing highly volatile components, in flexible tube structures which are less subject to stress cracking, and are desirable for providing improved packaging structures. Such products include those containing methyl salicylate. It is also seen that the invention provides a multiple layer film comprising EVOH which is functional for providing a lesser degree of protection, in a much simpler structure, for products which are less demanding of the properties of the sheet material, while still providing excellent barrier in EVOH layer 514 to transmission of oxygen or methyl salicylate.

With the sheet materials of the illustrated embodiments having thus been disclosed, it is seen that several and various modifications may be made to the invention without departing from the spirit and scope of the concept. Thus the invention should be interpreted, not only with respect to the illustrated embodiments, but more appropriately in light of the appended claims.

Claims

1. A multiple layer sheet material, comprising:

(a) a first layer (12), of metal foil, having a first primed surface and a second surface;

(b) a second layer (14), of ethylene vinyl alcohol, having a first surface disposed toward the first foil layer and a second surface disposed away from said foil layer; and

(c) third adhesive means (20-24) between the first and second layers adhering them to each other.

2. A sheet material according to claim 1, including a fourth protective means (32) on or for the said second surface of said first, foil layer (12) and a fifth, covering layer (16) on or for the second surface of the second layer (14).

3. A sheet material according to claim 2, further including a sixth layer (18), of adhesive, between said second and fifth layers (14, 16) and wherein the third adhesive means (20-24) comprises a seventh adhesive layer (22) on said first surface of said second layer.

4. A sheet material according to claim 3, wherein the ethylene vinyl alcohol in said second layer comprises about 55 mole percent to about 72 mole percent vinyl alcohol moieties.

5. A sheet material according to claim 3 or claim 4, wherein the sixth layer (18) of adhesive comprises a base polymeric resin and anhydride comprising active anhydride component equivalent to between about 0.10% and about 0.60% maleic anhydride.

6. A sheet material according to claim 3, 4 or 5, wherein the sixth layer (18) of adhesive comprises a base polymeric resin and anhydride comprising active anhydride component equivalent to between about 0.13% and about 0.40% maleic anhydride and wherein the sheet material is capable of functioning, in a package made therefrom and containing a product having a component capable of attacking the interfacial adhesion between said first layer of metal foil and said third adhesive means in protection of said interfacial adhesion from being destroyed by said product component, such that said package is capable of holding said product over the normal shelf life of said product.

7. A sheet material according to claim 3, 4, 5 or 6, wherein the composition of the sixth adhesive layer (18) has a melt index, at 210 °C, of between 3 and 9.

8. A sheet material according to any of claims 3 to 7, wherein the composition of the sixth layer (18) includes up to 15% of a material which provides for physical bonding.

9. A multiple layer sheet material according to any of claims 3 to 8, wherein the composition of the seventh layer (22) comprises the composition of the sixth layer.

10. A multiple layer sheet material according to any of claims 3 to 7, wherein the composition of the sixth layer (18) includes up to 15% of a tackifying resin and wherein the composition of the seventh layer (22) comprises the composition of the sixth layer.

11. A multiple layer sheet material comprising a first layer (14, 514) of ethylene vinyl alcohol copolymer, a second layer (24, 519) comprising an olefinic polymer composition on a first side of said ethylene vinyl alcohol copolymer layer (14, 514), a third layer (16, 516) of linear low density polyethylene on a second side of said ethylene vinyl alcohol layer (14, 514) and a fourth adhesive layer (18, 518) between said ethylene vinyl alcohol layer (14, 514) and said third layer (16, 516) respectively.

12. A sheet material according to claim 11, further including a fifth adhesive layer (20) between said first and third layers (14 and 16).

13. A sheet material according to claim 12, wherein the compositions of said fourth and fifth layers (18, 20) comprise linear low density polyethylene and anhydride comprising active anhydride component equivalent to between about 0.13% and about 0.40% maleic anhydride.

14. A multiple layer sheet material comprising a first layer (14, 514) of ethylene vinyl alcohol copolymer having first and second surfaces, a second (24, 519) covering layer on said first surface of said ethylene vinyl alcohol copolymer layer, a third adhesive layer (18, 518) on said second surface of said ethylene vinyl alcohol copolymer layer (14, 514), the third adhesive layer comprising a linear low density polyethylene and anhydride comprising active anhydride component equivalent to about 0.13% to about 0.40% maleic anhydride, and having a melt index, at 210 °C, of between 3 and 9, and a fourth layer (16, 516) of linear low density polyethylene on the third layer (18, 518) opposite the first layer (14, 514).

15. A sheet material according to claim 14, wherein the second, covering layer (24, 519) comprises low density polyethylene adhered by an intervening adhesive layer comprising linear low density polyethylene.

16. A package made with a sheet material according to any of the preceding claims.

17. A package made with a sheet material of any one of claims 2 to 13, the fifth layer of the sheet material being disposed toward the inside of the package.

18. A package made with a sheet material according to claim 6 or claim 7, including therein a product, the latter having a component therein capable of attacking the interfacial adhesion between the metal foil and the third adhesive means, and wherein the portion of said sheet material between said product and said metal foil is capable of functioning in protection of said interfacial adhesion from being destroyed by said product component, and does function in protection of said interfacial adhesion from being destroyed by said product component.

19. A package made with a sheet material according to claim 6 or claim 7, wherein the composition of the sixth layer of said sheet material includes a base resin, and up to 15% of a material which provides for physical bonding, the package including therein a product, the latter comprising a component capable of attacking the interfacial adhesion between the metal foil and the third adhesive means, and wherein the portion of said sheet material between said product and said metal foil is capable of functioning in protection of said interfacial adhesion from being destroyed by said product component, and does function in protection of said interfacial adhesion from being destroyed by said product component.

20. A package according to claim 18 or claim 19, wherein the product contains a component selected from methyl salicylate, acetic anhydride, acetone, undecylenic acid, ichthamnol and polyurethane prepolymers.

21. A package made with a sheet material according to any one of claims 11 to 15, and including therein a product comprising a volatile component selected from methyl salicylate, acetic anhydride, acetone, undecylenic acid, ichthamnol, and polyurethane prepolymers, and wherein the sheet material is functional to retard transmission of the volatile component through the sheet material, sufficient to provide for normal compositional stability of the volatile component in the product over the normal shelf life of the product.

22. A package comprising a packaging sheet material and as product comprising a volatile component selected from methyl salicylate, acetic anhydride, acetone, undecylenic acid, ichthamnol, and polyurethane prepolymers, the packaging sheet material comprising, from the inside surface of said sheet material in said package outwardly, a first layer (16, 516) comprising an olefin polymer or copolymer, a second, adhesive layer (18, 518) comprising a polyethylene and anhydride comprising active anhydride component equivalent to about 0.13% to about 0.40% maleic anhydride, and having a melt index, at 210 °C, of between 3 and 9, and a third layer of ethylene vinyl alcohol (14, 514), the packaging sheet material being functional to retard transmission of the volatile component through the sheet material sufficient to provide for normal compositional stability of the volatile component in the product over the normal shelf life of the product, the composition of said first layer for example being based on propylene, ethylene or a combination of propylene and ethylene.

23. A package comprising a multiple layer packaging sheet material, and a product contained in said package and functionally in contact with said packaging sheet material, the product containing a volatile and chemically hard-to-hold component, such as methyl salicylate, acetone, acetic anhydride, undecylenic acid, ichthamnol of polyurethane prepolymer, and the packaging sheet material comprising a first layer (14, 514) of ethylene vinyl alcohol copolymer and a second layer (18, 518), comprising an adhesive polymer composition, adhered in surface-to-surface contact to said first layer of ethylene vinyl alcohol copolymer and positioned between that layer and said product, said adhesive polymer composition comprising a linear low density polyethylene and about 0.10% to about 0.60% maleic anhydride.

24. A package according to claim 23, wherein the second layer adheres the said first layer to a third polymer layer (16, 516) comprising an olefinic polymer selected from ethylene polymers and copolymers, propylene polymers and copolymers, butylene polymers and copolymers, including polyisobutylene, and combinations of the above polymers and copolymers.

25. A method of making a package, comprising:

(a) fabricating a sheet material by adhering a first layer (32) of a covering material to a second layer of metal foil (12) and, on the surface of said foil opposite the said first layer, adhering, by use of intervening adhesive means (20-24), a coextruded film structure comprising at least three layers and including a layer of ethylene vinyl alcohol copolymer, and a heat sealable layer (16) on the surface of the coextruded structure opposite said foil layer (12), the coextruded film structure being between about 0.035 mm and about 0.30 mm thick;

(b) fabricating the sheet material into a package enclosure by bringing portions of said sheet material in facing relationship and heat sealing contiguous portions thereof, leaving a side or end of said package open;

(c) placing a product in the package; and

(d) closing the said side or end of the package, to complete the fabricating, filling, and sealing of the package.

26. A method according to claim 25, wherein the product contains a component capable of attacking the interfacial adhesion between the metal foil layer and the intevening adhesion means, and wherein the ethylene vinyl alcohol in the coextruded film structure comprises at least about 55% vinyl alcohol, and an adhesive layer on one surface of said ethylene vinyl alcohol layer, the said adhesive layer comprising a polyethylene and anhydride comprising active anhydride component equivalent to about 0.10% to about 0.60% maleic anhydride.

27. A method according to claim 25 or claim 26, wherein the fabricating step (b) either comprises forming a sachet or pouch structure with fin or lap seams (54), or comprises forming a tubular structure with a lap seal (50).

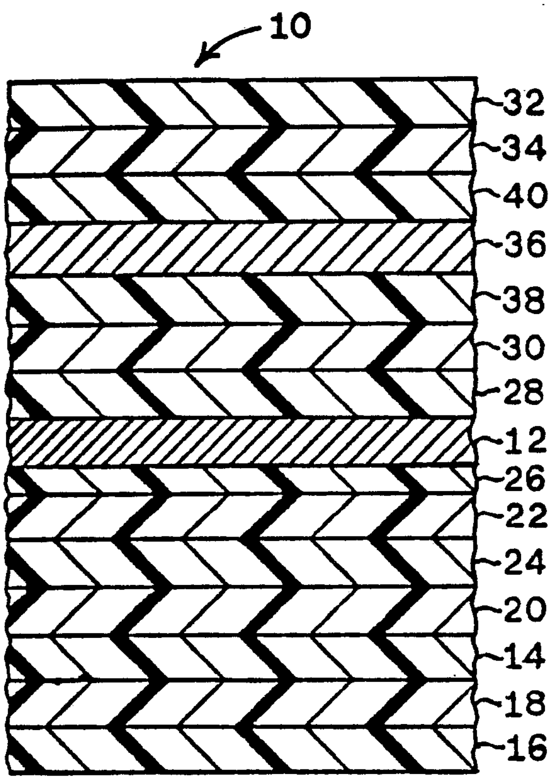

FIG. 1

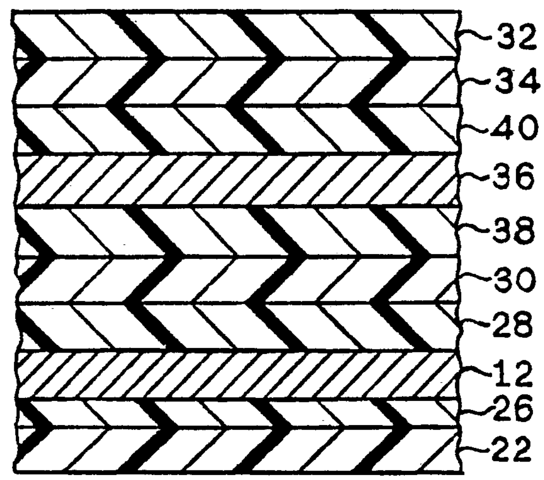

FIG.1A
PRIOR ART

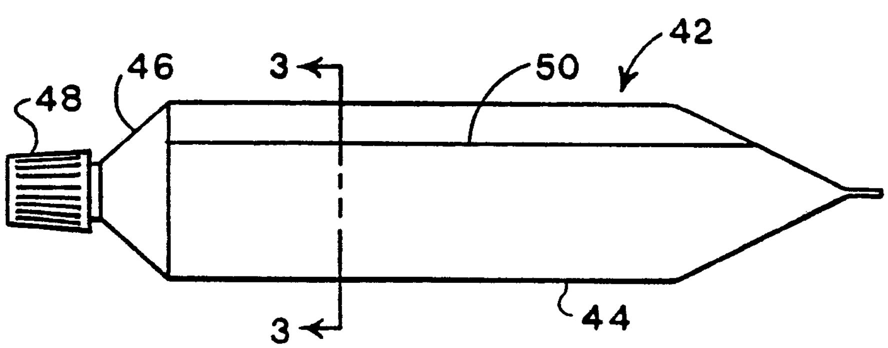

FIG. 2

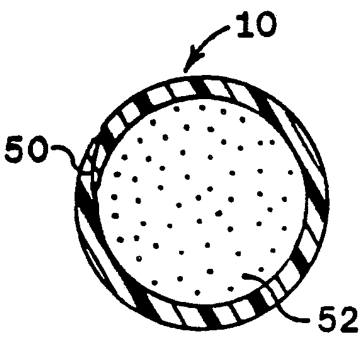

FIG. 3

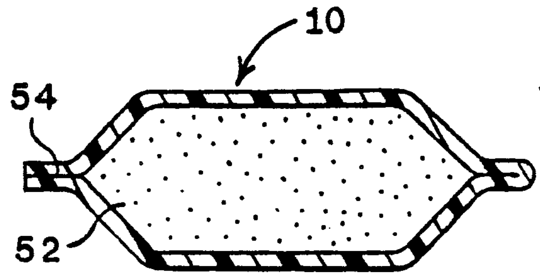

FIG. 4

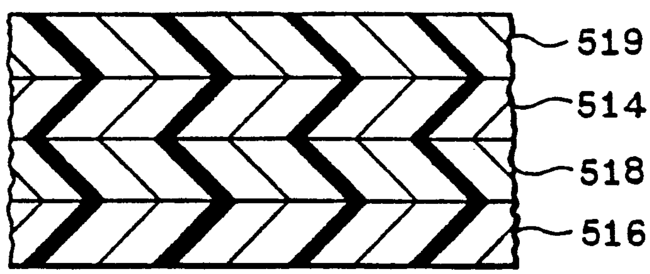

FIG. 5